Wet air oxidation for the treatment of solid wastes generated on autarkic sites

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Industrial effluents have variable compositions depending on the industry: refineries, pharmaceuticals, distilleries, food processing, paper mill… The most widespread treatment of effluents containing organic pollutants is the biological way, but microorganisms are unsuitable in the case of refractory or toxic products. Legislations regulate more and more severely the management of these wastes and favor the development of alternative processes allowing to treat effectively particular pollutions, as in pre-treatment before a biological process or for a complete degradation of organic matters in carbon dioxide and in water. Other technologies are under research and development, as for instance Wet Air Oxidation (WAO), especially for wastewaters that contains high chemical oxygen demand.

WAO or hydrothermal sub-critical oxidation was developed at first by the company ZIMPRO (Zimmermann, 1950) in the United States. The first WAO process allowed the synthesis of vanillin from liquid residues of paper mill industry. In the years 1960-1970, Sterling (which detained ZIMPRO patents) developed low temperature processes to treat various types of waste (urban, agricultural, regeneration of active carbon, etc.). It is in the 80s that WAO knows a renewed interest as treatment method for residual liquids, because of new regulations at the world level for environmental protection. WAO aims at oxidizing the organic fraction of an aqueous effluent by contacting organic pollutants with an oxidizing agent. WAO processes work mostly in conditions of temperature ranging from 100 to 320°C and a total pressure (of air or pure oxygen, according to the choice of the oxidizer) of 0,5 to 20MPa (Luck, 1979; Kolaczkowski *et al*, 1999). The oxidation yield is about 70 to 95% with a residence time of 30min to several hours. The 5 to 30% of organic matter which are not totally transformed into the liquid phase are mainly in the form of acetic acid, formic acid and other volatile fatty acids. That is why most of WAO units are followed by a biological treatment to degrade these acids. In these operating conditions, the solubility of oxygen in water is more important than in the ambient conditions and favors degradation kinetics of the organic fraction in carbon dioxide and water. Andreozzi *et al* (1999) suggest that this technology is the most adapted solution for the aqueous effluents having a COD included between 20 and 200g.L^{-1} what corresponds in approximately 1 to 10% of organic matter. From 20g.L^{-1}, the heat necessary for the functioning of the process is supplied by the exothermicity of the oxidation reaction and beyond 200g.L^{-1}, the amount of oxidizer becomes too important and generate higher costs (compression of the oxidizer, etc.) that makes incineration more attractive.

Autarkic sites (ships, oil rig, isolated communities,) generate liquid waste streams (black/gray water, cooking greases, oils, infirmary discharges) and solid (catering waste, paper, cardboard, plastics) containing organic matter, that are often stored for longer or shorter periods, then transported and incinerated by specialized companies. The recent scientific literature is dense about the experimental studies in laboratory on WAO of simple organic compounds or more complex effluents, on the use of catalysts allowing to lower the conditions of pressure and temperature. However, all these studies do not supply enough information to design this process to industrial scale. On reaction aspects, this work consists to run experiments with oxygen concentration conditions suitable for designing an industrial treatment unit. For that purpose, kinetic studies are conducted with an initial total organic carbon (TOC) concentration about 3g.L^{-1} of solid wastes. The different solid wastes are chosen for these experiments because it is often found in real wastes (canteen food wastes, can film packaging, corn flakes package, water bottle). The oxygen excess chosen for the experiments (70% excess of oxygen) is realistic contrary to 1000–2000% of excess found in literature (Baillod *et al*, 1991; Portela *et al*, 1997).

The reactor used for this study is made of stainless steel 316L (Figure 1). The autoclave has the following characteristics: 30 MPa maximum pressure, 350°C maximum temperature, 200cm^3 internal volume. The temperature in the cell is kept stable by a hot (electric power)/cold (double jacket with air or water) regulating system. The stirring device is a Rushton type mixer with eight blades, with a hollow shaft allowing a recirculation by extraction of the gas phase into the liquid phase. A motorized pump allows the introduction of fluids inside the reactor. A dip tube at the bottom of the reactor allows to take samples at regular intervals during the experiments.

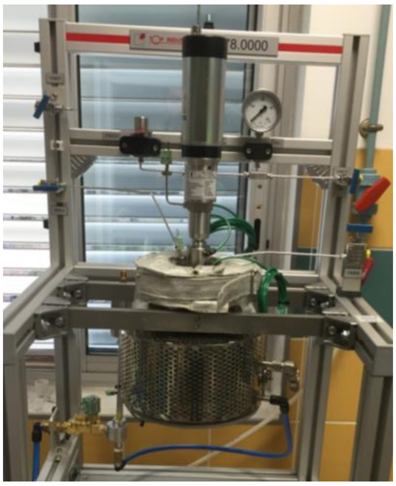

Figure 1. WAO experimental apparatus

For WAO experiments, the autoclave is charged with $60cm^3$ of waste and first pressurized with nitrogen. When the required temperature is reached, the pump is filled with air (oxygen/nitrogen mixture) and pressurized to an exceeding pressure of 40MPa. Opening the supply valve of the reactor designates the beginning of the reaction. Preliminary calculations permit to fix an excess of oxygen of 70% and the initial phenol/oxygen stoichiometry is constant for each tested temperature. The mixing speed is set at 800rpm. The reaction evolution is monitored by analyzing samples by TOC measurement by a Shimadzu TOC analyzer VCPH. The calibration of total carbon and inorganic carbon is made from mother solutions at 1000ppm. Two experiments were carried out for each operating condition, to verify the reproducibility and to have for each waste TOC reduction curves as a function of time with points every 15min. The operating conditions and TOC reduction are synthesized in Table 1 for every waste.

Table 1. TOC reduction and operating conditions for WAO experiments on solid wastes

Waste	Temperature (°C)	Pressure (MPa)	Maximum TOC reduction (%)
Food wastes	200-300	10-15	95
Grey&black water simulant	200-300	10-15	96
Paper & cardboard	200-300	10-15	96
Plastic packagings	200-300	10-15	97
Plastic bottles	200-300	10-15	97

The results obtained show that WAO is a high-performance alternative for the destruction of organic solid and liquid waste generated on autarkic sites. The experimental data obtained (operating conditions, TOC reduction) will be used to carry out a techno-economic feasibility analysis for the implantation of WAO unit on this kind of site, with an environmental comparison (done by life cycle analysis methodology) with the conventional solution.

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